NOTE

Mechanistic Studies of CH_4/O_2 Conversion over SiO_2-Supported Nickel and Copper Catalysts

In this note, we report the reaction behaviors of CH_4 and CH_4/O_2 (2/1) with reduced and unreduced SiO_2-supported copper and nickel (10 wt% metal) catalysts in a pulse microreactor at 600, 650, and 700°C.

Methane utilization has received much attention in the past few years. Besides the methane oxidative coupling process, the partial oxidation of methane to syngas is another route being considered. The reaction is mildly exothermic and the catalysts employed are mainly supported Group VIII metals such as Ni, Rh, Ru, Pd, Pt, and Co (1–8). Usually, a H_2/CO ratio of about 2, suitable for methanol and Fischer–Tropsch syntheses, is obtained. Until now, a unified viewpoint on the mechanism of this catalytic process has not been reached. Many researchers (1, 2, 7–9) believed that two stages are involved in the process: (i) complete oxidation of methane to CO_2 and H_2O and (ii) reforming of the remaining methane by H_2O and/or CO_2 formed in the first stage. Furthermore, Lunsford and co-workers (2) proposed that the initial complete oxidation reaction occurs on the unreduced NiO/Al_2O_3 catalyst and the reforming reactions happen on the reduced Ni/Al_2O_3 catalyst. Schmidt and co-workers (4, 5, 10) have shown that syngas ($H_2:CO$ very close to 2:1) can be produced at ca. 1100°C with high H_2 and CO selectivities (>90%) and high CH_4 conversion (>80%) over Pt- or Rh-coated alumina monoliths by direct catalytic oxidation of methane with oxygen. The reaction was conducted at residence times between 10^{-2} and 10^{-4} s, noticeably shorter than the time of ca. 1 s (4, 11) usually adopted in a steam reforming reactor. With such short superficial contact time, they considered that the direct oxidation reaction should be independent of the reforming reactions and concluded that the primary surface reaction is methane pyrolysis followed by surface carbon oxidation and H_2 desorption. Choudhary *et al.* (12, 13) reported that high selectivity to CO and H_2 could be achieved at temperature lower than 700°C (in some cases, as low as 300–400°C) on a variety of Ni- and Co-containing catalysts with high reactant gas space velocities ($10^5–10^6$ h^{-1}) and concluded that syngas was formed directly from methane oxidation. However, Matsumura and Moffat (8) pointed out that the amount of reactants fed in Schmidt's and Choudhary's studies was so large that the heat generated during the exothermic reaction would facilitate methane reforming via CO_2 and H_2O. Lunsford and co-workers (14) proved the existence of a large thermal gradients (as much as 300°C) or hot spots within the catalyst bed in the oxidation of methane at high space velocities using an optical pyrometer and pointed out the temperature reported by Choudhary *et al.* was in fact much less than the true temperature of the catalyst.

In order to avoid the augmentation of catalyst bed temperature, a pulse technique was used to probe the mechanistic aspects of the conversion of CH_4/O_2 to syngas (15). Previously, we reported the pulse studies of CH_4 and CH_4/O_2 over unreduced NiO/Al_2O_3 catalysts at 500°C and pointed out that the adsorption of CH_4 on reduced nickel is a key step for the formation of syngas. In the present studies, the reaction behaviors of CH_4 and CH_4/O_2 with SiO_2-supported copper and nickel catalysts were compared in view of the fact that the former catalyst demonstrates an ability of causing methane complete oxidation while the latter is known to be active in syngas formation. The contrast of the two will provide insights into the mechanisms of the CH_4/O_2-to-syngas reaction. To avoid gas-phase reforming reactions, the highest reaction temperature was kept to 700°C.

The SiO_2-supported copper and nickel catalysts (with 10 wt% metal) were prepared by impregnating SiO_2 granule (Aldrich, 60-80 mesh) with the corresponding nitrate (BDH, A.R. grade) solution followed by drying at 100°C for 12 h and annealing at 500°C for 2 h for decomposition. The catalysts so prepared are the unreduced ones and are signified as NiO/SiO_2 and CuO/SiO_2. The catalysts treated in H_2 for one hour at 500°C are the reduced ones and are expressed as Ni/SiO_2 and Cu/SiO_2.

The reaction was carried out in a pulse microreactor (15). The reactor was made of quartz tube with 4 mm i.d. A chromel–alumel thermocouple was introduced from the top of the reactor and placed in the middle of the catalyst bed to measure the reaction temperature. For each study, 50 mg of catalyst was used. The pulse volumes of CH_4, O_2 and CH_4/O_2 (2/1) were 1.11, 0.44, and 1.03 ml, respectively. The reactants and products were analyzed on-line by a Shimadzu GC-8A gas chromatograph equipped with TCD
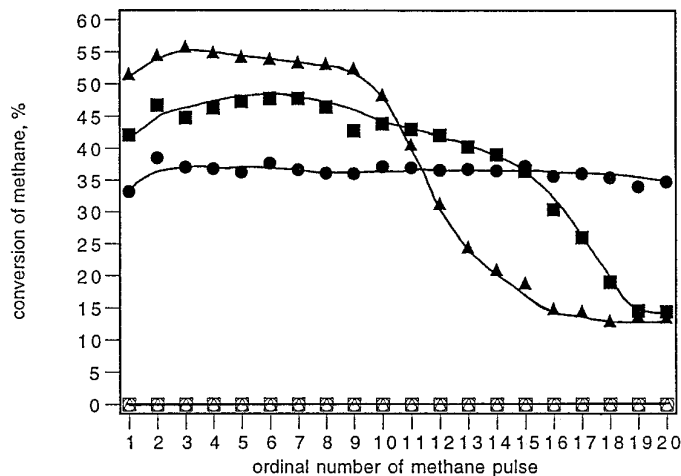
FIG. 1. The relationship of CH_4 conversion to the ordinal number of CH_4 pulsing over Ni/SiO_2 (solid symbols) and Cu/SiO_2 (hollow symbols) at 600°C (○), 650°C (□), and 700°C (△).

(MS5A and Porapak Q as columns, 50°C; helium as carrier gas). Selectivities (mol%) were calculated on the basis of carbon contents in the products. In the CH_4/O_2 experiments, the results of carbon balance are estimated to be within 5% accuracy. In the absence of the catalysts, the blank runs showed almost no activity in the reaction conditions mentioned in this paper.

Methane (99.9%), oxygen (99.7%), hydrogen (99.995%), and helium (99.995%) from Hong Kong Oxygen Company were used directly without further purification.

As shown in Fig. 1, no methane conversion was detected when methane was pulsed over Cu/SiO_2. This is a definite indication that metallic copper is ineffective in dissociating methane. Over Ni/SiO_2, however, methane dissociated, and a large amount of H_2 and a trace amount of CO were detected. Initial CH_4 conversion was ca. 55% at 700°C. It started to decline rapidly after the 8th pulse and stayed at around 15% after the 15th pulse. At 650°C, the CH_4 conversion was initially about 45% and declined gradually after the 8th pulse and reached ca. 15% at the 19th pulse. At 600°C, the CH_4 conversion stayed at around 35% within the first 20 pulses. Other than H_2 and CO, no C_2 hydrocarbons were observed as gaseous products.

CO and CO_2 were formed when O_2 was pulsed in instead after the 20th pulse of CH_4 over Ni/SiO_2, indicating that there were carbon species deposited on the catalyst. Reduction treatment after the complete removal of the accumulated carbon by oxidation could restore the catalyst to its original activity for methane decomposition. So the occupancy of the active sites by carbon species should be the reason for the decline in methane dissociation activity. Maybe, the missing of C_2 hydrocarbons as gaseous products is a hint for the complete decomposition of methane to give C(s) and H(s). The combination of two H(s) would

generate $H_2(g)$ and the oxidation of C(s) by pulses of oxygen would generate CO and CO_2. Based on the amount of CO and CO_2 generated and the volume of each oxygen pulse, we obtained the molar ratio of surface carbon to oxygen at each reaction point. As shown in Fig. 2, the molar ratio of surface carbon to oxygen decreased with the ordinal number of oxygen pulse. At each temperature, at the reaction points where the surface carbon to oxygen ratio was above 1, the selectivities of CO and CO_2 were fairly stable (<5% of fluctuation), and the selectivity of CO increased with increasing temperature. When the mo-
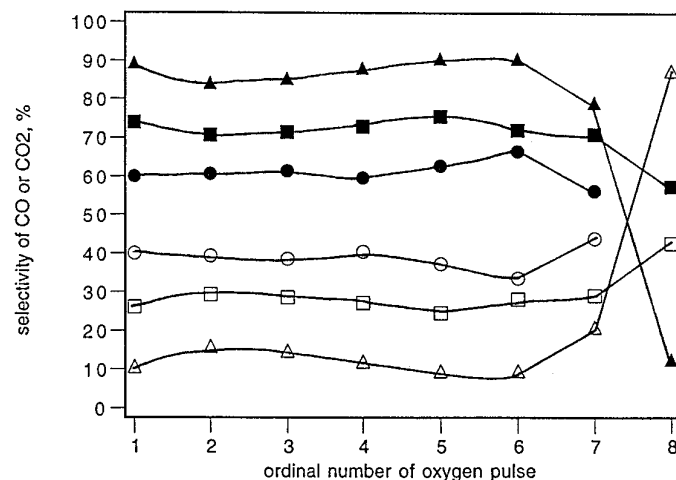
(a)
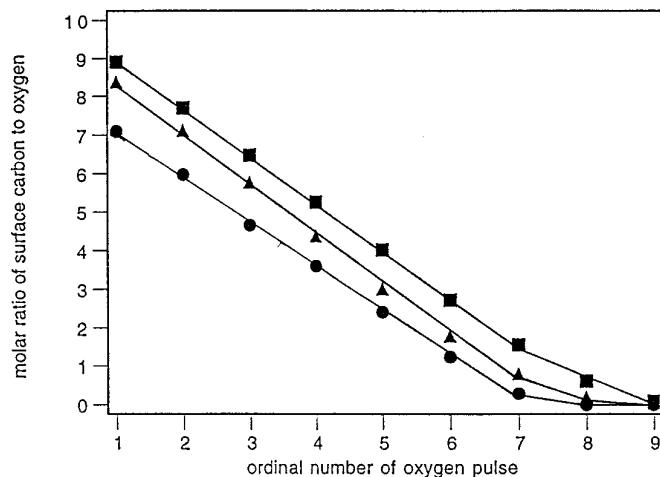
(b)

FIG. 2. The relationship of (a) molar ratio of surface carbon to oxygen and (b) CO (solid symbols) and CO_2 (hollow symbols) selectivities with the ordinal number of O_2 pulsing over Ni/SiO_2 after the pulsing of CH_4 shown in Fig. 1 at 600°C (○), 650°C (□), and 700°C (△).
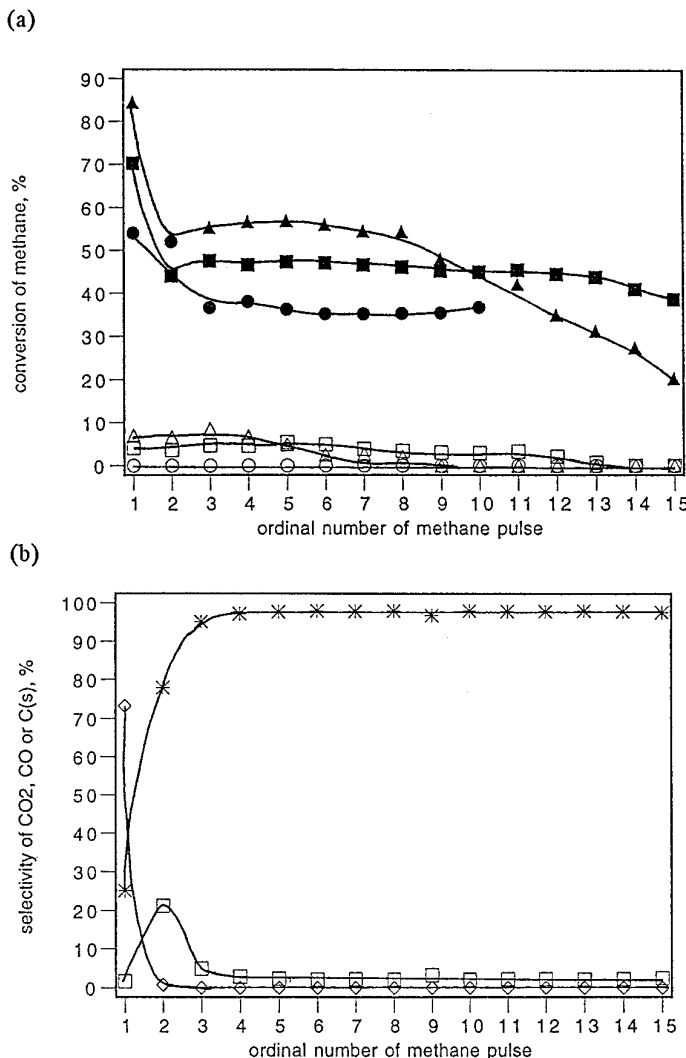
(a)

(b)

FIG. 3. (a) The relationship of CH_4 conversion to the ordinal number of CH_4 pulsing over NiO/SiO_2 (solid symbols) and CuO/SiO_2 (hollow symbols) at 600°C ($\bigcirc$), 650°C ($\square$), and 700°C ($\triangle$). (b) The relationship of CO_2 ($\diamond$), CO ($\square$), and C(s) ($\ast$) selectivities to the ordinal number of CH_4 pulsing over NiO/SiO_2 at 650°C.

lar ratio of surface carbon to oxygen decreased to 0.3, 0.6, and 0.8 respectively at 600, 650, and 700°C, the corresponding CO selectivity at each temperature decreased by only ca. 10% in value. The results indicated that with molar ratio of surface carbon to oxygen >1, the product distribution in the oxidation of surface carbon is subject to the change of reaction temperature.

Figure 3a shows that CH_4 did not interact with CuO/SiO_2 at 600°C. At 650 and 700°C, only a small amount of methane was converted to CO_2 and H_2O. Since there was no oxygen in the reactant feed and the reaction of CH_4 occurred on the support alone was negligible, the generation of CO_2 and H_2O must be the result of CH_4 interaction with lattice oxygen of CuO. In other words, lattice oxygen

of CuO are active sites for methane complete oxidation. Such saying is compatible with the result of Efstathiou *et al.* (16), who, after following the reaction of CH_4/He with the 2 wt% Li_2O/TiO_2 catalyst used for the oxidation coupling of methane (OCM), pointed out that lattice oxygen of TiO_2 are sites for methane complete oxidation.

Over NiO/SiO_2, regardless of the reaction temperature, methane conversion at the first CH_4 pulse was higher than the following pulses. The gaseous products were H_2, H_2O, CO_2, and CO. The accumulation of carbon on the surface was verified by the detection of CO and CO_2 when O_2 was pulsed over the catalyst after the pulsing of CH_4, and its amount at each reaction point of methane pulse was obtained based on 100% carbon balance. The changing profiles of the selectivities of CO_2, CO, and C(s) as related to the ordinal number of CH_4 pulsing were similar at the temperatures studied and only the profile at 650°C is shown in Fig. 3b. At the first pulse of methane, the selectivities of CO_2, C(s), and CO were respectively ca. 73, 25, and 2%. Hence initially, the interaction of CH_4 with NiO/SiO_2 involved mainly the complete oxidation of methane (and hence the reduction of Ni^{2+} to Ni^0) to give prevailingly CO_2. Based on the initial weight of the catalyst and the amount of CH_4 consumed as well as the amount of CO_2 and CO formed in the first two reaction points of methane pulses, it can be estimated that all the NiO initially present has been reduced to Ni^0. From the 3rd pulse onward, the main reaction was methane decomposition on the reduced nickel sites and the methane converted ended up mainly as C(s) (ca. 97% selectivity).

The reaction for the direct interaction of methane with lattice oxygen over CuO/SiO_2 and NiO/SiO_2 can be represented as

$$CH_4(g) + 4M^{2+} + 4[O^{2-}] \rightarrow$$
$$CO_2(g) + 2H_2O(g) + 4M^0 + 4[\ast], \quad [1]$$
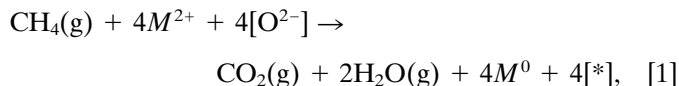
where M denotes Ni or Cu and [*] denotes the oxygen anion vacancy.

The products of $CH_4/O_2(2/1)$ interaction with CuO/SiO_2 and NiO/SiO_2 at 600, 650 and 700°C were exclusively CO_2 and H_2O. As shown in Fig. 4, over both CuO/SiO_2 and NiO/SiO_2, at each reaction temperature, the conversion of O_2 was approximately four times that of CH_4, indicating the overall reaction proceeds according to $CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$. From Fig. 4a, one can see that at equal temperature, methane conversion over NiO/SiO_2 was higher than that over CuO/SiO_2, implying that lattice oxygen of NiO is more reactive. With the rise in reaction temperature, the amount of methane converted increased distinctively over CuO/SiO_2, whereas over NiO/SiO_2, methane conversion remained roughly at 28%. Figure 4b shows that the trend of oxygen conversion over CuO/SiO_2
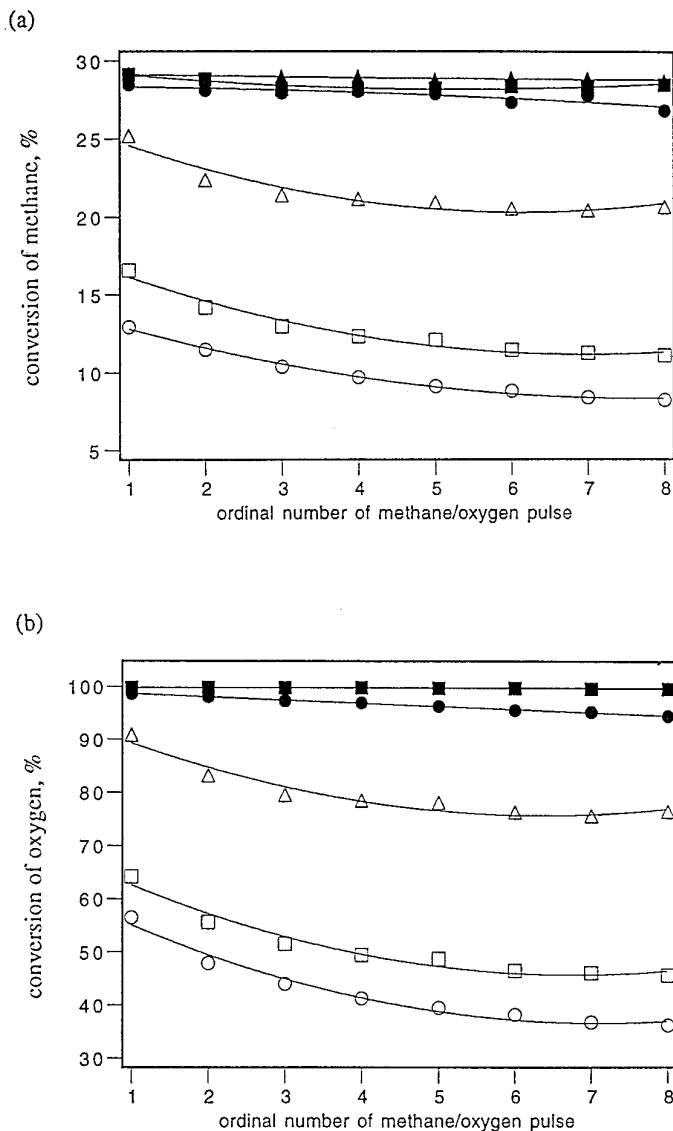
(a)

(b)

FIG. 4. The relationships of (a) CH_4 and (b) O_2 conversions to the ordinal number of CH_4/O_2 pulsing over NiO/SiO_2 (solid symbols) and CuO/SiO_2 (hollow symbols) at 600°C ($\bigcirc$), 650°C ($\square$), and 700°C ($\triangle$).

and NiO/SiO_2 is very similar to that of methane conversion with the rise in reaction temperature. Therefore, a parallel relationship can be drawn between the conversions of methane and oxygen over the two catalysts.

Since other than CO_2 and H_2O, CO and H_2 were not observed during the interaction of CH_4/O_2 with the two unreduced catalysts, it can be concluded that steam and CO_2 reforming reactions had not taken place. Also, the parallel relation between the conversions of methane and oxygen indicates that proportional amount of gaseous oxygen was used to replenish the lattice oxygen consumed during the complete oxidation of methane. It can be inferred that under the conditions adopted in our studies,

the interaction of CH_4/O_2 with CuO/SiO_2 and NiO/SiO_2 follows something like the redox or/and push–pull mechanism suggested for CO oxidation (17):

1. Direct interaction between methane and surface lattice oxygen to give CO_2, H_2O with the catalysts partially reduced according to reaction [1].

2. Reaction of gaseous oxygen with Cu^0 and Ni^0 to regenerate Cu^{2+} and Ni^{2+}, restoring the catalysts to their original states:

$$2M^0 + 2[*] + O_2(g) \rightarrow 2M^{2+} + 2[O^{2-}]. \qquad [2]$$
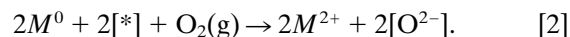
Under similar conditions, methane conversion over Ni/SiO_2 was significantly higher than that over Cu/SiO_2 (Fig. 5a). An increase in reaction temperature would result in the increase in CH_4 conversion over both reduced catalysts. Independent of temperature rise, oxygen conversion over Ni/SiO_2 remained constantly at 100%. Over Cu/SiO_2, it dropped from 100% at the first pulse to 37, 51, and 73% at the 8th pulse at 600, 650, and 700°C respectively (Fig. 5b).

Similar to the reaction of CH_4/O_2 over CuO/SiO_2, the gaseous products over Cu/SiO_2 were exclusively CO_2 and H_2O. A comparison between Figs. 4a,4b and 5a,5b reveals that except for the first four pulses of CH_4/O_2, the amount of methane and oxygen converted over Cu/SiO_2 and CuO/SiO_2 was very similar. It can be deduced that during the first four pulses of CH_4/O_2 over Cu/SiO_2, gaseous oxygen was consumed in the oxidation of Cu/SiO_2 to CuO/SiO_2 (hence higher in conversion). After the 4th pulse, the reaction over Cu/SiO_2 became one over CuO/SiO_2. This is verified by the fact that CO_2 and H_2O were formed when CH_4 was pulsed over Cu/SiO_2 after the eighth pulse of CH_4/O_2. However, over Ni/SiO_2, the main products were CO, H_2 (selectivities >60%) with CO_2 and H_2O being the minor ones (Fig. 5c). In comparison, the reaction of CH_4/O_2 over Cu/SiO_2, which is inactive for methane dissociation and is easily oxidized to CuO/SiO_2 in the presence of O_2, led only to CO_2 and H_2O formation, while the reaction of CH_4/O_2 over Ni/SiO_2, on which methane adsorbs dissociatively, resulted in the formation of CO and H_2 as main products. The result indicated that methane dissociation is a key step for syngas formation.

In the reaction of CH_4/O_2 over Ni/SiO_2, CO selectivity increased with increasing reaction temperature (Fig. 5c). Based on the amount of methane converted and 100% of oxygen conversion at each reaction point, the molar ratio of surface carbon to oxygen was estimated to be ca. 1.1, 1.2, and 1.4 respectively at 600, 650, and 700°C in the reaction of CH_4/O_2 over Ni/SiO_2. As shown in Fig. 2, CO selectivity increased with increasing temperature in the oxidation reaction of surface carbon deposited on the Ni/SiO_2 catalyst when the molar ratio of surface carbon to oxygen was above one. The similar trend between CO
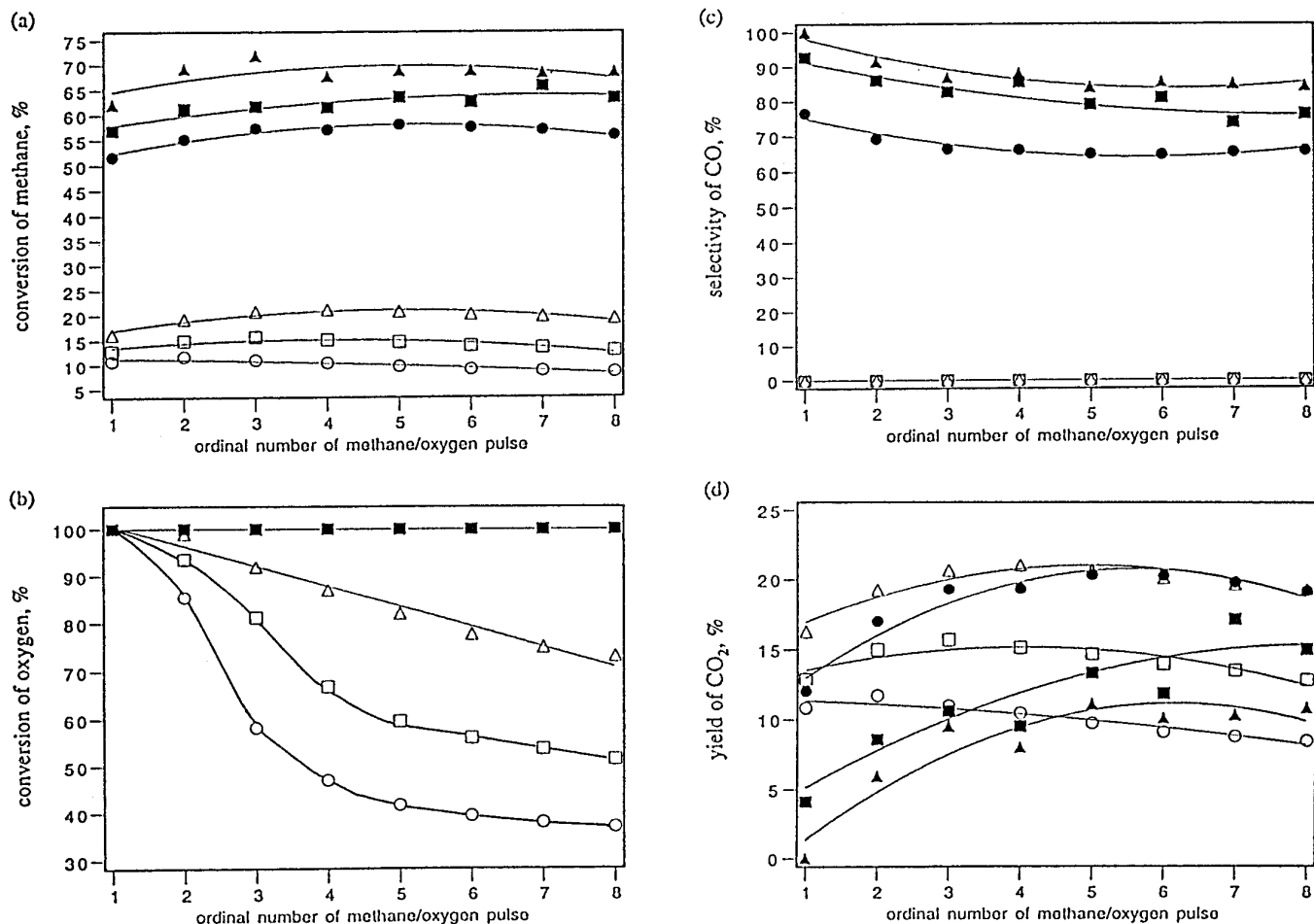
FIG. 5. The relationship of (a) CH_4 and (b) O_2 conversions, as well as (c) CO selectivity and (d) CO_2 yield, to the ordinal number of CH_4/O_2 pulsing over Ni/SiO$_2$ (solid symbols) and Cu/SiO$_2$ (hollow symbols) at 600°C ($\bigcirc$), 650°C ($\square$), and 700°C ($\triangle$).

selectivity and reaction temperature observed in the reaction of CH_4/O_2 and in the oxidation reaction of surface carbon over Ni/SiO$_2$ implied that the primary surface reaction of CH_4/O_2 over Ni/SiO$_2$ was methane pyrolysis, $CH_4(s) \rightarrow C(s) + 4H(s)$, followed by oxidation of C(s) to CO and combination of H(s) to H$_2$. Similarly, as Lunsford and co-workers (2) have reported, temporary stoppage of the CH_4 flow during the reaction of oxygen-deficient CH_4/O_2 mixture over a 25 wt% Ni/Al$_2$O$_3$ catalyst, resulted in reaction of the previously deposited surface carbon with the continuing oxygen feed, producing a CO/CO$_2$ mixture whose composition conformed to the thermodynamic equilibrium ratio at the reaction temperature employed.

Over Ni/SiO$_2$, the yield of CO_2 decreased with increasing temperature. Such trend became reversed over Cu/SiO$_2$ (Fig. 5d). The result indicates the formation of CO_2 over Ni/SiO$_2$ followed a mechanism other than that over Cu/SiO$_2$. In other words, reaction [1] was not the main pathway for CO_2 formation over Ni/SiO$_2$. Further oxida-

tion of carbon monoxide is probably the main pathway for CO_2 formation and the selectivity of CO is mainly governed by the two competitive steps, namely, the oxidation of CO(s) to give CO_2 and the desorption of CO(s) to CO(g). As calculated using the Bond Order Conservation–Morse Potential approach (18), over Ni(111) surface, the oxidation of CO(s) to give CO_2(s) has an activation energy of 64kJ/mol, while the value for CO(s) desorption is 113 kJ/mol. Since the activation energy of CO(s) desorption is nearly double that of CO(s) oxidation, the augmentation of reaction temperature would favor CO(s) desorption more than CO(s) oxidation, leading to the increase in selectivity of CO. This is what we have observed over the Ni/SiO$_2$ catalyst.

Over Ni/SiO$_2$, oxygen and methane adsorbed competitively on metallic nickel. Though a small amount of metallic nickel might be oxidized to Ni^{2+} in the presence of oxygen, the oxidized nickel can be rereduced via reaction [1]. Thus a certain amount of Ni^0 sites can be sustained to keep the

formation of CO and H_2 going. Methane adsorption on Ni is an activation process and the adsorption rate is accelerated exponentially by temperature raising, whereas the surface coverage of O(s) adatoms decreases with rising temperature. Thus, one can expect the higher the temperature is, the higher the ratio of Ni^0/Ni^{2+} will be. The coexistence of Ni^0 and Ni^{2+} sites on nickel catalysts for syngas formation from CH_4/SiO_2 had been confirmed by XPS and XRPD studies by Lunsford and co-workers (2).

In summary, we have avoided the ''hot spot'' problem by employing the pulse method in the mechanistic studies of methane partial oxidation to syngas. Under the experimental conditions adopted, reactions due to gas-phase steam and CO_2 reforming were negligible.

Methane does not interact with Cu/SiO_2 but adsorbs dissociatively on Ni/SiO_2 to give H_2 and surface carbon. Methane interaction with CuO/SiO_2 produces CO_2 and H_2O, whereas over NiO/SiO_2 the products are CO_2, H_2O, H_2, surface carbon, and a small amount of CO. The interactions of CH_4/O_2 with CuO/SiO_2, NiO/SiO_2, and Cu/SiO_2 generate exclusively CO_2 and H_2O. Only in the reaction of CH_4/O_2 over Ni/SiO_2, on which methane adsorbs dissociatively, would CO and H_2 be formed as main products. We conclude that lattice oxygen are sites responsible for methane complete oxidation. Methane dissociation over metallic nickel is a key step for CO and H_2 formation. In other words, the conversion of CH_4/O_2 to syngas over nickel catalysts at temperatures below 700°C follows the pyrolysis mechanism.

ACKNOWLEDGMENT

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C. T. Au[*,1]
H. Y. Wang[*,†]
H. L. Wan[†]

* Department of Chemistry
Hong Kong Baptist University
224 Waterloo Road
Kowloon, Hong Kong
† The State Key Laboratory for
Physical Chemistry of the Solid Surface
Xiamen University
Xiamen 361005
People's Republic of China

[1] To whom correspondence should be addressed.